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Final Report

**Proof-of-Concept: Assembly of Carbon Nanocrystals for Ordered 3D
Networks**

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Proof-of-Concept: Assembly of Carbon Nanocrystals for Ordered 3D Networks

1. Introduction

One-dimensional (1D) carbon nanotubes (CNTs) have attracted many attentions and demonstrated exceptional properties, while two-dimensional (2D) graphene sheets also demonstrated numerous outstanding performances, including similar mechanical, electrical, and thermal properties to 1D CNTs. Particularly, graphene sheets exhibit huger specific surface area, due to the nature of 2D nanostructures. It is anticipated to take advantage of both CNT and graphene's strength through assembling 1D CNTs and 2D graphene sheets into a novel ordered 3D network with CNTs perpendicularly bonded to the graphene plane, as illustrated in Figure 1. This novel carbon structure is expected to generate many exciting properties. For example, CNTs show excellent thermal conductivity along longitude direction and graphene exhibits exceptional thermal conductivity in plane, and then this new 3D structure provides a perfect way for heat dissipation from electronic circuits and devices. In addition, this novel architecture has great potential for energy storage application. Large specific surface area and nonporous structure will enable physisorption-based hydrogen storage with high capacity, fast absorption and de-absorption of hydrogen. Hence, this novel 3D architecture opens numerous opportunities for thermal management, renewable energy, structural materials, electronic devices and other industrial applications.

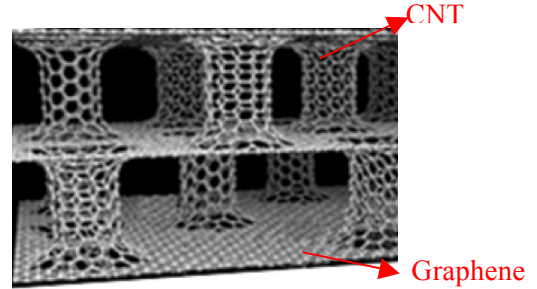


Figure 1. Illustration of novel 3D network

However, it is very challenging to fabricate such an ordered hybrid architecture consisting of graphene and CNTs due to the difficulty in manipulating such nanoscale building blocks. Graphene sheets usually randomly distributed and it is difficult to orient them. The CNT lengths range from a few hundred nanometers to several micrometers, and this length distribution posts a significant challenge to assemble the proposed 3D network. The most difficult issue is to orient CNTs and graphene sheets simultaneously so that all the CNTs are perpendicularly bonded to the graphene sheets. It is also difficult to tailor the density of CNTs vertically “grown” in the graphene sheets in the novel 3D architecture. Due to these challenges, no experimental attempt toward this novel structure has been found even though a simulation effort was reported in 2008.

2. Objectives and goals

The objective of this project is to explore the feasibility for fabricating a novel ordered 3D architecture of CNT/graphene, which consists of alternatively stacked vertically-aligned 1D CNTs and horizontally-aligned 2D graphene sheets.

3. Illustration of assembly process

In this project, the 3D CNT/graphene networks were assembled through transferring vertically aligned CNT arrays on the graphene surface through tailored binders. Since the vertically aligned CNT arrays are usually grown on the silicon substrate and CNT arrays are not able to free stand, it is difficult to transfer the CNT arrays to the graphene film while the CNT array morphology is maintained. Therefore, the big challenge of transferring CNT arrays to graphene layer for 3D ordered network lies in the interfacial bonding between graphene/CNT arrays. This interfacial bonding force should be strong enough to peel off CNT arrays from the substrate, in which the CNT arrays are grown by the CVD method. In this project, we investigated the feasibility of assembling CNT array to graphene via tailored bonding for 3D ordering carbon nanotube networks. In this project, a ultra-thin poly(methyl methacrylate) (PMMA) was coated to ~50nm graphene film. At the elevated temperature, the melting PMMA penetrated into the CNT array, and then created a strong mechanical bonding between graphene surface and CNT array after cooling down to the room temperature, resulting in easy transferring of CNT array to graphene surface for assembly of 3D network. The details for process were illustrated in the Figure 2.

Vertically aligned CNT arrays were produced by chemical vapor deposition (CVD). Graphene was produced by exfoliation from graphite flakes and its aqueous suspension was filtered and washed with melamine solution for 3 times to increase the mechanical performance. Subsequently, the filtered graphene film was immersed into acetone to etch the filter membrane, and the resultant freestanding graphene film was loaded on to the Teflon/glass fiber film, and attached onto the glass slide with scotch tape. The PMMA was spin-coated onto the graphene film. Then, the PMMA-coated graphene film was turned over and placed on another Teflon film. The first Teflon film will be removed and then another PMMA layer will be coated. Removal Teflon film resulted in PMMA-sandwiched graphene membrane.

Subsequently, the original CNT array was placed on the PMMA coated silicon wafer under the pressure of 8MPa at 250 °C for 10 minutes. After the sample was cooled down, the silicon substrate

was easily detached, and another PMMA coated graphene was placed on the transferred CNT array with same pressure and heat parameter, resulting graphene/CNT array/graphene 3D networks. Then repeating the above process led to multi-floor CNT/graphene networks.

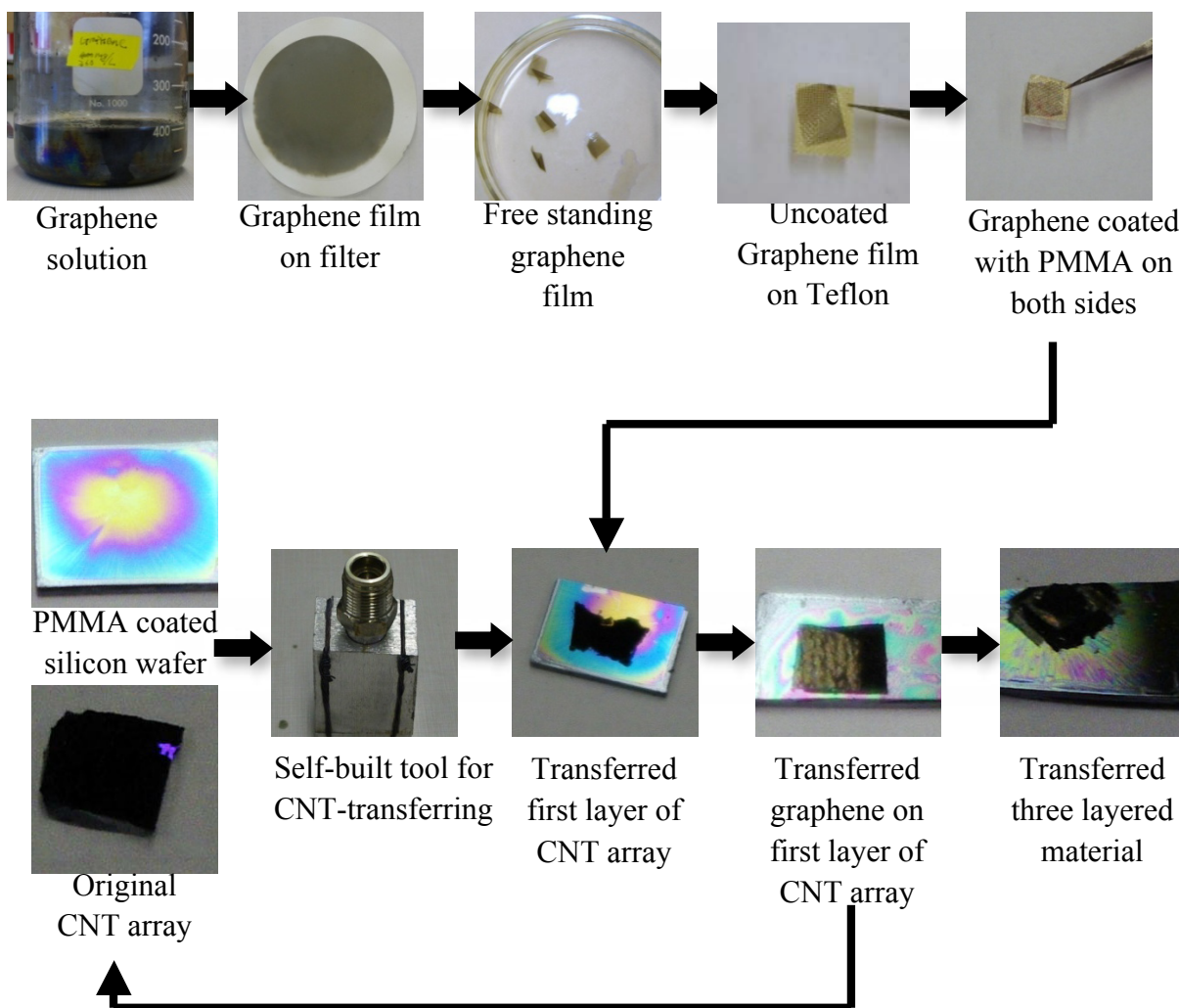


Figure 2 Illustration of assembling 3D network of CNT/Graphene

4. Graphene fabrication

Graphite natural flakes were chemically intercalated by modified Hummers method and then exfoliated with by ultrasonic processing under pH=10, which is adjusted by ammonia. Subsequently, the exfoliated graphene oxide is reduced by hydrazine hydrate at a mass ratio of 7:10 (hydrazine to graphene oxide) at 95 °C for 24 hour. The resulted graphene sheets were filtered and washed with deionized water thoroughly and then characterized by transmission electron microscope and the results are shown in Figure 3. Some of them are monolayer graphene while the others are few-layer graphene sheets. The graphene solution was further subjected to centrifugation process at 3000rpm for 30min and the supernatant solution was collected and characterized, as shown in Figure 2(b). Almost of them were in monolayer states.

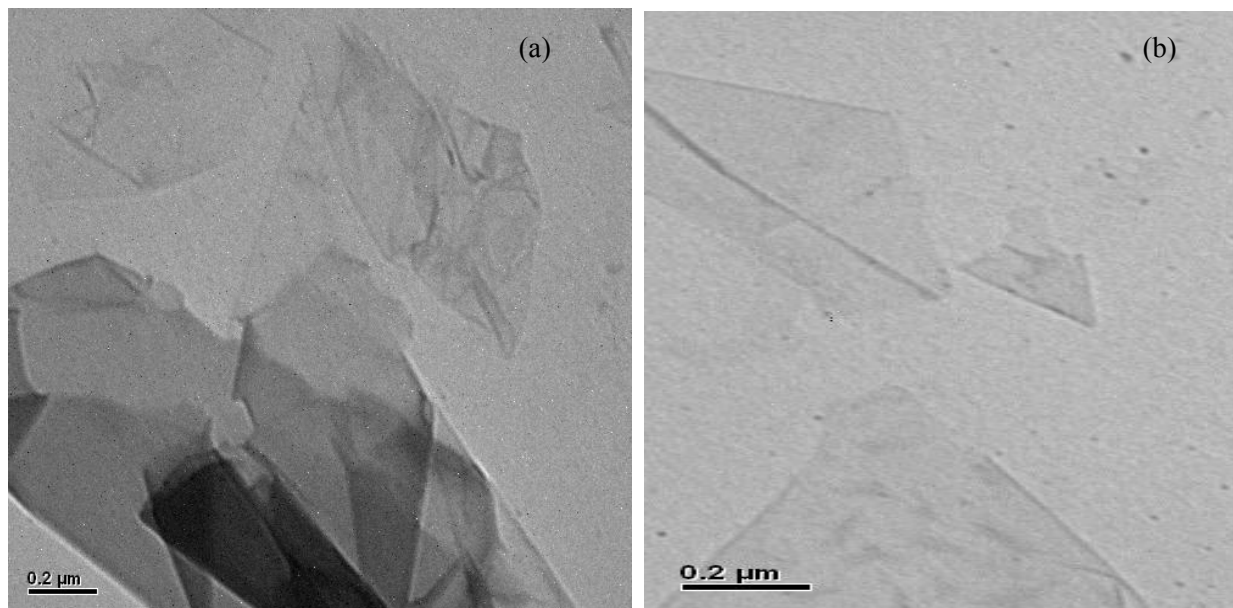


Figure 3 TEM images of graphene sheets. (a) Graphene sheets before centrifugation and (b) graphene sheets after centrifugation.

As-produced graphene oxide and graphene were also characterized by Raman spectroscopy, and the results are shown in Figure 4.

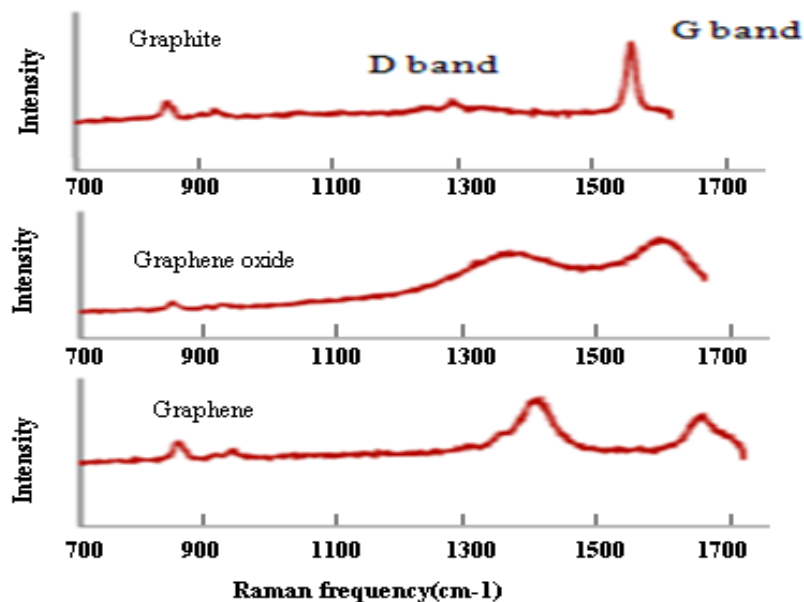


Figure 4 Raman spectra of graphite, graphene oxide and graphene

For the graphite, a sharp G-band was observed at around 1580cm^{-1} and the D band intensity was almost zero. Graphene oxide showed a broad and small G band. Reduced graphene showed a much smaller G-band. The I_D/I_G of graphite is close to zero, I_D/I_G of graphene oxide is 0.91 and I_D/I_G of graphene produced hydrazine reduction is 1.16. Hence, graphene produced from chemical exfoliation exhibited significant defects.

Around 100nm-thick graphene film was fabricated through filtration of 100uL of the graphene solution with a concentration of 1.3mg/mL and followed dissolving of filter membrane. The resultant transparent graphene film was shown in Figure 5.

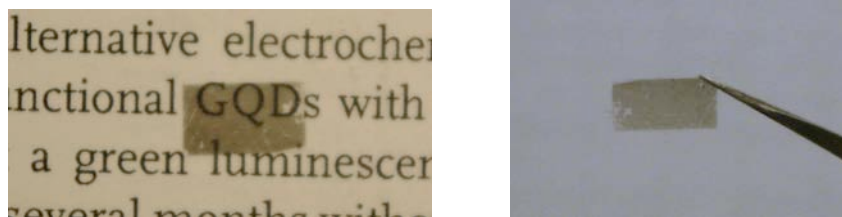


Figure 5. Photo image of the 100nm-thick graphene film

5. Assembly of CNT/Graphene 3D network

The CNT array and graphene were bonded via the PMMA binder coated on the graphene surface, and thus, the PMMA thickness should be critical for the successful transferring CNT array to the graphene film. Simple calculations were carried out to investigate the effect of the thickness of PMMA coating and structure of the vertically aligned CNT array (VA-CNT).

5.1 Detaching forces for CNT/silicon substrate

Lahiri et al studied the bonding force between CNT bundle and substrate [1] by employing an atomic force microscope (AFM) probe to slide the surface of the CNT array and peel them off. The parameters in their work are given as follows: AFM tip radius=200 nm, CNT diameter= 70 nm, CNT density= $38 \times 10^{13}/\text{m}^2$, and then the measured force for detaching a bundle of CNT from a silicon substrate is 30uN. Therefore, the bonding force between the single CNT and substrate was calculated as follows:

$$F_{\text{single-detach}} = \frac{F_{\text{array-d}}}{N} = \frac{F_{\text{array-d}}}{d \times A} = 0.628 \text{uN}$$

Where $F_{\text{single-detach}}$ denotes the detach force of single CNT from the substrate; N is the number of CNT; $F_{\text{array-d}}$ denotes the force to detach the whole array; the symbol d represents the area density of CNT array and A represents the effective contact area.

Given that the length of C=C bond in the hexagonal ring is around 0.144 nm, the number of the carbon atoms in the interface can be estimated and the interfacial bonding force between CNT and silicon substrate can be calculated for the CNTs with different diameters. For the CNT with diameter of 10nm and 20nm, respectively, the interfacial bonding forces were estimated as follows:

$$F_{\text{single atom-sub}} = \frac{F_{\text{single-detach}}}{M}$$

where $F_{\text{single atom-sub}}$ denotes the single atom bonding force with the substrate; M represents the amount of atoms contacting the substrate.

For D=10nm CNT,

$$F_{\text{single CNT-sub}} = F_{\text{single-detach}} \times M_{10\text{nm}} = 0.089 \text{uN}$$

For D=20nm CNT,

$$F_{\text{single CNT-sub}} = F_{\text{single-detach}} \times M_{20\text{nm}} = 0.178 \text{uN}$$

Therefore, the detaching force is also proportional to the amount of carbon atoms contacting the substrate. In this project, the CNT diameter is around 10nm.

5.2 Bonding forces of CNT/graphene

Another factor, which should be determined, is the bonding force between the CNT and graphene through the PMMA binders. This bonding force should be strong enough to transfer CNT array to the graphene surface. PMMA was coated to the graphene surface and will serve as the binders to help transfer CNT array. The embedding length of CNTs in the PMMA may significantly affect the transferring –based assembly. We estimated the binding force between the CNT/PMMA as a function of CNT diameters and embedded length according to Carole A. Cooper’s results [2]. The equations in our calculation are given as follows:

$$S_{embedded\ CNT} = \pi r^2 L \quad (1)$$

$$S_{single\ hexagonal\ ring} = 3L_{c-c}^2 \sin 60 \quad (2)$$

Where the $S_{embedded\ CNT}$ stands for the area of CNT embedded in the polymer; r is radius of the CNT; L denotes the embedded length; $S_{single\ hexagonal\ ring}$ is the area of a single hexagonal ring; L_{c-c} is the carbon bond length.

In the Cooper’s study, the diameter of CNT was 8.2nm and embedded length was 484nm, and then the embedded surface of CNT can be calculated to 12410.536nm^2 . Assuming the delocalized carbon bond length is 0.144nm (between single carbon bond and double carbon bonds), the area of single hexagonal ring was calculated to 0.0287nm^2 .

Given that there are two carbon atoms in one hexagon ring, the number of carbon atoms in interface can be calculated by the following equation:

$$N_{carbon\ atoms} = 2 \frac{S_{embedded\ CNT}}{S_{single\ hexagonal\ ring}} \quad (3)$$

Combining the results attained from equation (1) and (2), the calculated number of carbon atoms in interface was derived to 864002. Then, the calculation of the force between single carbon atom and epoxy polymer can be derived from the following equation:

$$F_{single\ carbon\ atom_epoxy} = \frac{F_{pull\ off}}{N_{carbon\ atoms}} \quad (4)$$

Therefore, we derived the force between the single carbon atom and epoxy to $4.398137 \times 10^{-12}\text{N}$;

Because of the difference in electro negativity between epoxy polymer and PMMA, the CNT/PMMA bonding force can be determined from the equation(5):

$$F_{carbon\ atom-PMMA} = 2.5F_{carbon\ atom-epoxy} \quad (5)$$

Therefore, the force between CNT and PMMA can be estimated by substituting equation (5) into the following equation:

$$F_{carbon-PMMA-sum} = F_{carbon\ atom-PMMA} \times N_{carbon\ atoms} \quad (6)$$

For CNT diameter of 10nm and 20nm respective, the binding force between CNT/PMMA was calculated as a function of embedded length, and the results are shown in Figure 6.

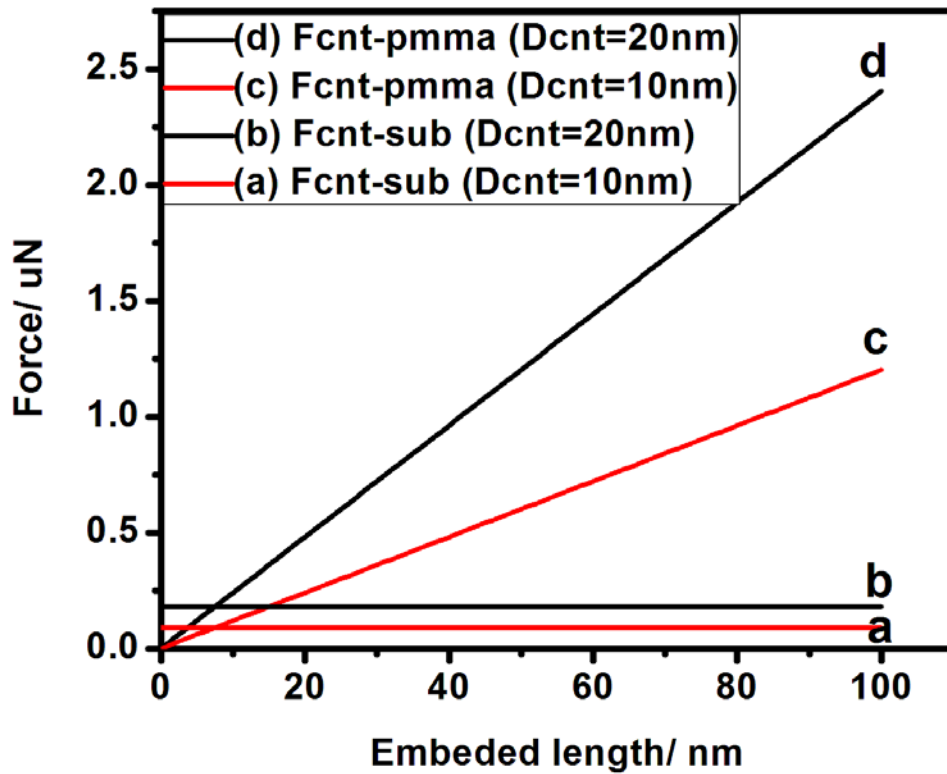


Figure 6. Binding force between single CNT/substrate and CNT/PMMA coating

According to the Figure 6, Increasing-embedding length of CNT in PMMA will increase the binding force of CNT/PMMA, and then it should be easy to transfer CNT array to the graphene surface. For a successful transferring, the minimum embedded CNT length in PMMA is ~8nm for the CNT with diameter of 10nm while it is 15nm for the CNT with diameter of 20.

5.2 PMMA thickness effect on the assembly

The theoretical calculations indicated that VA-CNT was able to peel-off from the original silicon substrate when the PMMA coating is as thin as 10nm. However, a thicker PMMA coating is indispensable due to the coating surface uniformity and mechanical behaviors. When the PMMA coating is thinner than 80nm, the Young's module significantly decreased. It changes from 4GPa for 80nm PMMA film to 0.5 GPa for 10nm PMMA film, as shown in the Figure 7 a [3]. Furthermore, the original uncoated graphene film is not as smooth as we assumed, and the AFM characterization of graphene film is shown in the Figure 7 b. The surface roughness is as high as 70nm.

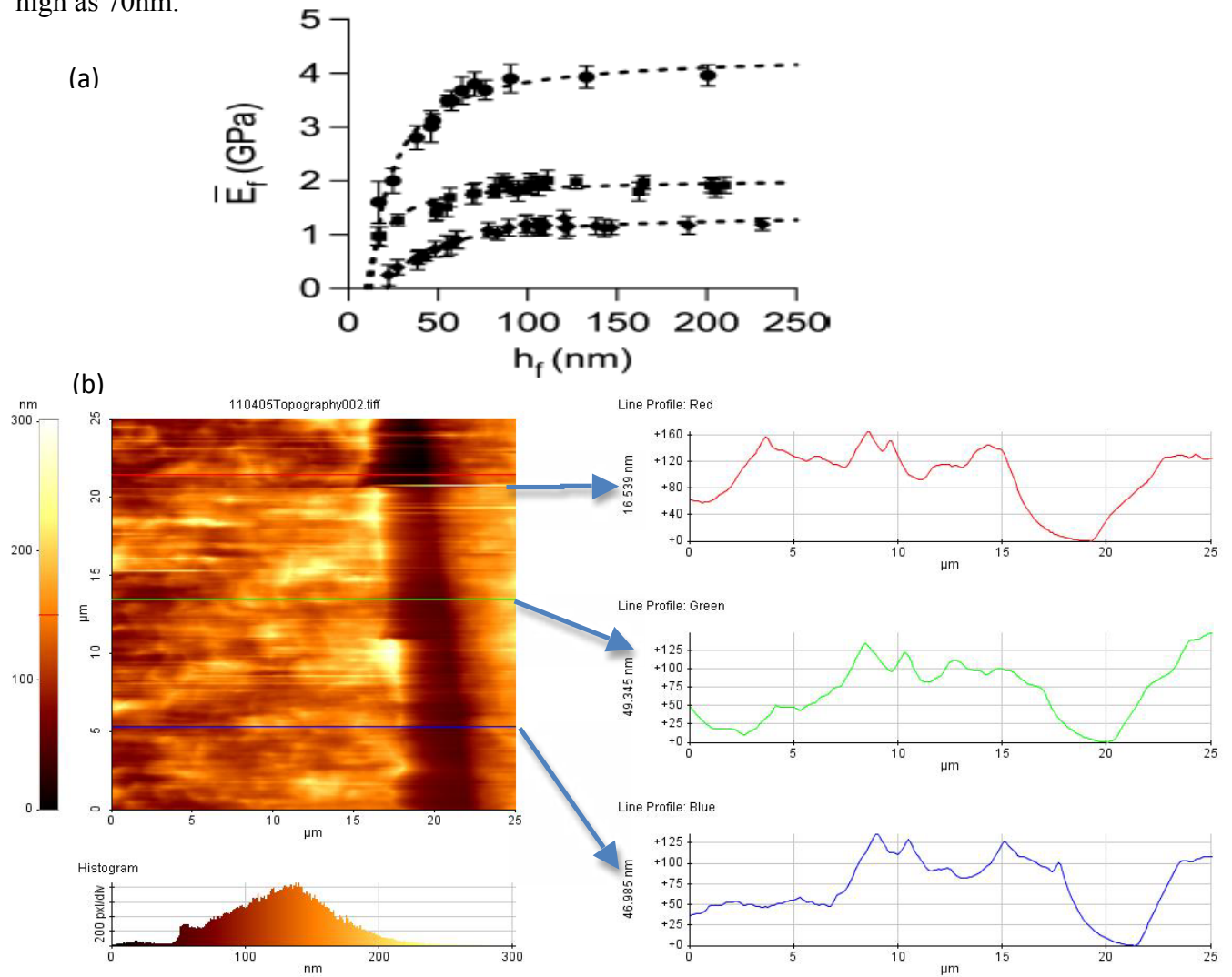


Figure 7(a) Modulus of PMMA as a function of thickness and(b) Graphene film roughness

Since the roughness of graphene film was as high as 70nm, 100nm PMMA film was coated onto the graphene surface for by the following spinning coating parameters: 5000 rpm for 5seconds followed by 7000 rpm for 25seconds. The resultant coating was characterized by scanning electron microscope (SEM), as shown in Figure 8. It was found that a 100nm PMMA was not uniform on the graphene film, and it can not cover the whole surface sine some graphene edges were exposed, as shown in Figure 8. In this case, CNT array was not able to completely transferred, and the CNT arrays were partially collapsed due to the non-uniform binding force. The resultant CNT array/graphene 3D network is shown in Figure 8(b).

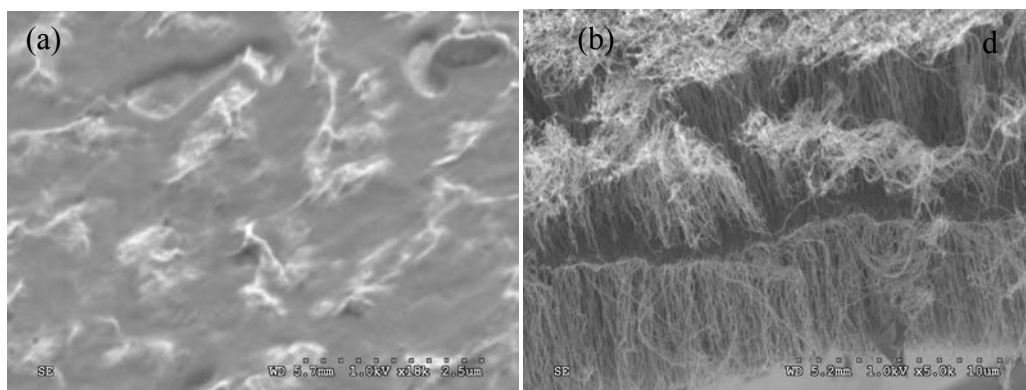


Figure 8(a) 100nm PMMA-coated graphene, (b) assembly results based on 100nm PMMA-coating

As we decreased the spinning speed to 5s X 4000 rpm followed by 25s X 6000 rpm, it is interesting to find that the graphene film was entirely covered by the PMMA coating, which was measured to be around 150nm thick. In order to confirm the existence of graphene between PMMA coatings, we partially peeled off the PMMA coating by a tape and then characterized it by SEM. The image is shown in the Figure 9, the graphene between two layers of the PMMA coatings was clearly observed and the rough surface of the graphene film was tightly attached to the PMMA coating.

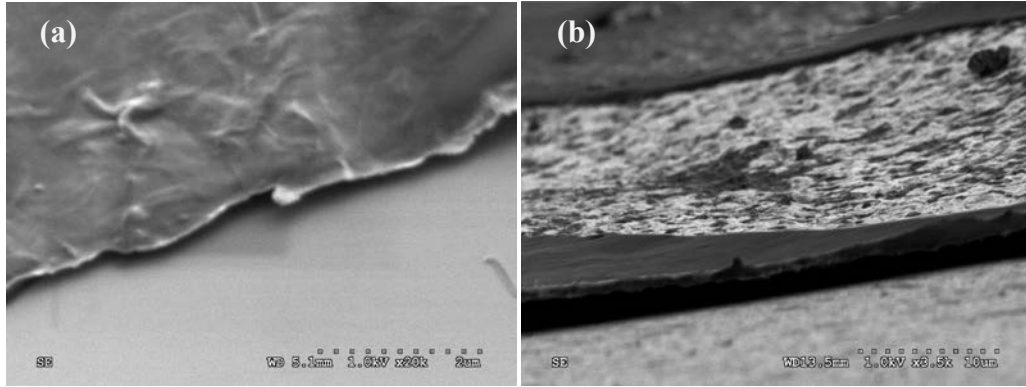


Figure 9 (a) graphene paper entirely coated with PMMA on both sides and (b) graphene/PMMA paper with PMMA partially peeled off.

5.3 Effect of contact pressure on the assembly

Contact pressure is also critical for the transferring CNT array to the graphene surface for assembly of 3D network. This pressure should be larger than the Young's module of the melting PMMA; otherwise, the CNT cannot be inserted into the PMMA at the elevated temperature. However, the pressure cannot be too large because large contact pressure usually bends CNT array or even make array collapse. We employed the 13MPa for transferring CNT array, and the VA-CNT was already severely bent. Some was collapse on the very top; most importantly, it makes impossible to assembly subsequent CNT arrays. The results are shown in Figure 10. When the contact pressure is decreased to the 8MPa, which is still much larger than the Young's module of melting PMMA. As-assembled 3D carbon nanotube network is shown in Figure 10. The CNT array can be effectively transferred while the CNT array was not significantly bent. No collapse of array was observed. Some vertical CNTs may be mildly curved, however, these curves can be recovered when the contact pressure was released. Therefore, a threshold contact pressure for successful assembly of CNT/graphene network was found to 8MPa.

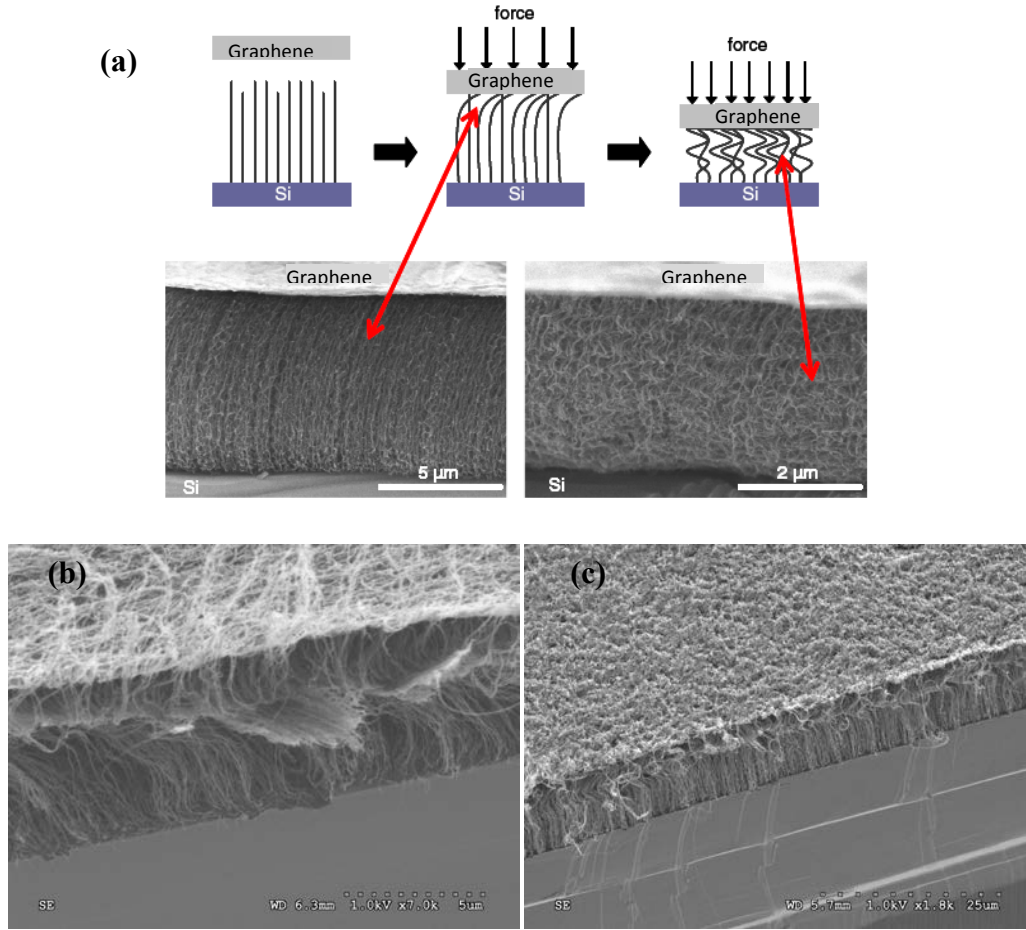


Figure 10 (a) Illustration of the effects of pressure on the original structure of the VA-CNT [4]; (b) SEM of VA-CNT after applying the pressure of 13MPa and CNT array was partially collapsed; (c) SEM of VA-CNT after applying the pressure of 8MP and no collapse was observed

5.4 Characterization of as-fabricated 3D network

The original VA-CNT was characterized by SEM, as shown in Figure 12. After the CNT array was transferred to the graphene surface, it was characterized by SEM again. No defect or bending of CNT can be found, and the thickness of the array was around 50μm. The successfully transferred VA-CNT onto PMMA coating at 250°C is shown in the Figure 12b. Even though the contact pressure during the transferring was as high as 8MPa, the alignment of VA-CNT was well maintained. Only a very small amount of collapse happened in the edge. Besides, the height of the VA-CNT array was decreased a little bit after transferred onto the PMMA. There are two possible reasons for this phenomenon. First, the VA-CNT may be inserted deeply into the PMMA coating; second, the VA-CNT was bent under the pressure during the transferring.

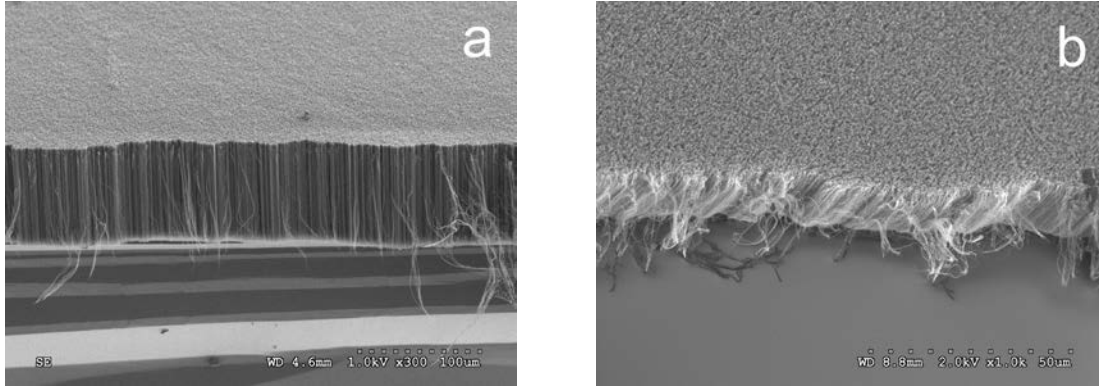


Figure 12 (a) original vertically aligned CNT array; (b) the first layer of transferred VA-CNT

In order to test the alignment stability of the VA-CNT during the transferring process, we compressed VA-CNT array on PMMA at the pressure of 8MPa. The results showed that as long as the force was kept in the vertical direction, the vertical structure of the CNT array was still well maintained, and the collapsing only can be found at the edges. After the first layer of the VA-CNT was successfully transferred, we further transferred the graphene and the second layer of VA-CNT on to it. The resulted structure was presented in the Figure 13.

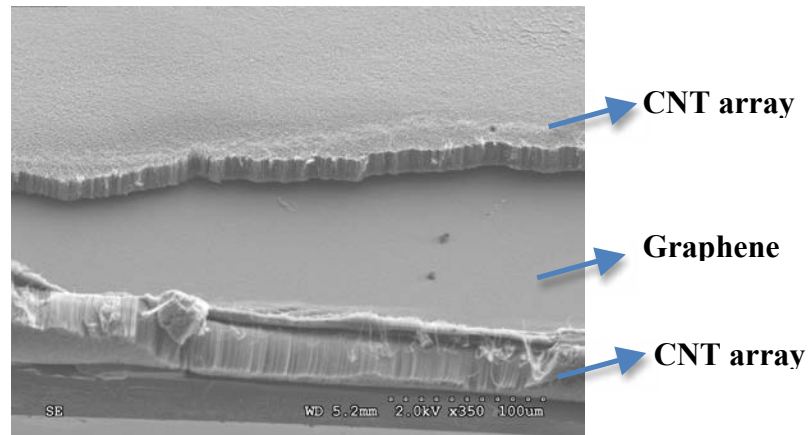


Figure 13 SEM of the assembled two-layered VA-CNT/graphene

The two-layered structure can be clearly observed in the image. The edges of the different layers were not aligned and step-like morphology was observed in the assembled 3D CNT/graphene network because the manual alignment was not precise at micro scale. In addition, because of the uneven pressure allocating on the edge (this only happened on the edges), the VA-CNT array exceeded the range of the silicon wafer, and the outside edge of VA-CNT wrapped up. Once again, because of the alignment issue, the graphene/PMMA layer was entirely covered by the second VA-CNT layer. Therefore, the graphene layer may not be seen in the SEM image.

Based on two-layered CNT/graphene network, the three-layered structure of the VA-CNT/graphene was further assembled, as shown in Figure 15. Each layer of CNT array was obvious observed while graphene layer was inserted between each two neighbored CNT arrays. The SEM image of three-layered CNT/graphene network has confirmed the successful assembly. The details of each layer are in the Figure 15 (b), (c) and (d), respectively. From the enlarged image of the first layer in Figure 15 (b), part of the VA-CNT edges collapsed; however, most of VA-CNT maintained their alignment and uniform height (see in Fig 15 a). In addition, the flat and smooth PMMA-coated graphene film was observed on the top of first layer. The original structures of the second and third layers of the VA-CNT were also well kept, which are shown in Figure 15 (b) and (c). The height of the CNT array decreased a little bit because of the uneven force distribution on the edge. Meanwhile, because of the relative small area of the third layer, the larger pressure was centered on a small area of the second-layer of CNT array, resulting in partially curved CNTs. Even so, the whole height was still around 50 μ m.

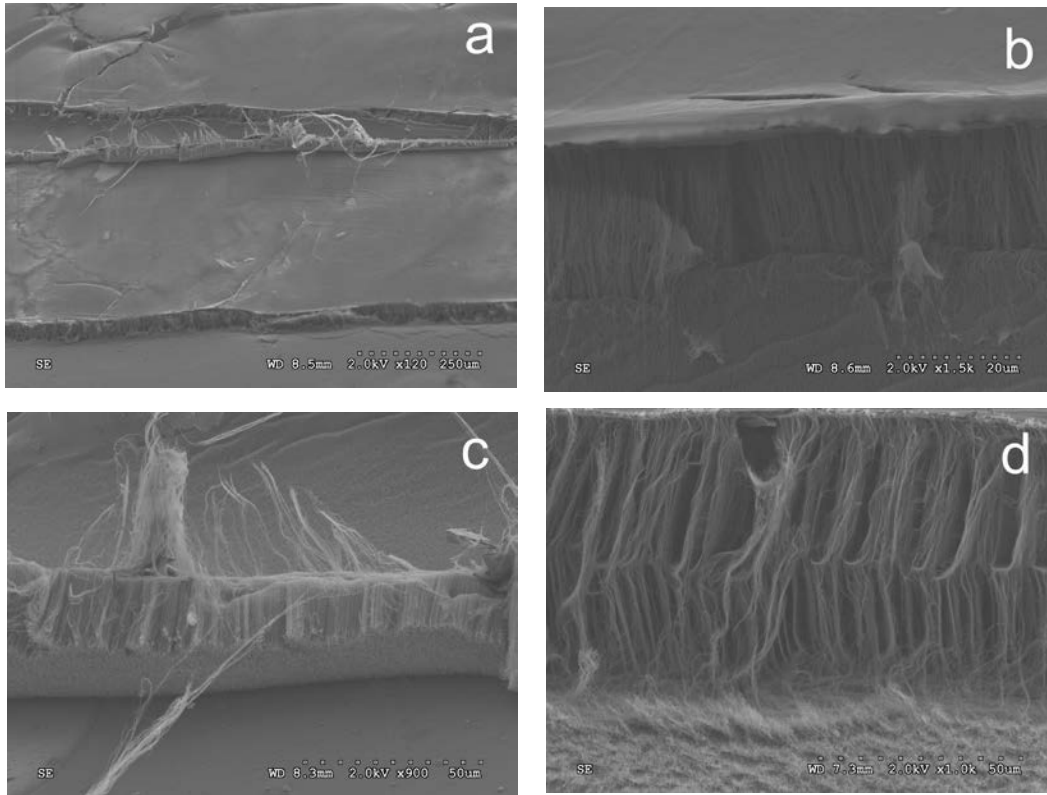


Figure 15 SEM of the transferred three-layered VA-CNT/graphene. (a) the over view of the three layered structure; (b), (c) and (d) are the details of the first, second and third layer, respectively.

6. Conclusions

In this work, we successfully assembled multi-layered VA-CNT/Graphene 3D network, in which the vertical aligned carbon nanotubes and graphene films were alternatively stacked by a PMMA binder. The optimal contact pressure was found to 8MPa while the PMMA binder was found to be above 150nm for successful assembly. In the as-fabricated novel 3D structures, the structures of the vertically aligned CNT array is well maintained, and almost all the single nanotubes are separated with each other, resulting in desired porosity and large surface area. When the VA-CNTs were well embedded in the PMMA, which was coated onto the graphene surface, and then tightly connected to the graphene after penetration through the PMMA coating during the assembly process. This may enable the whole structure conductive in the both vertical and horizontal directions. Further work will be carried out to characterize the specific surface area of the as-assembled 3D network and the potential for hydrogen storage will be examined. In addition, the thermal conductivity of this 3D network will be also studied by the three-omega test. The effect of CNT morphology and CNT/graphene interface on thermal conductivity will be studied. What is more, ultra-small conductive nanoparticles (such as 5nm silver nanoparticles) will be dispersed into PMMA at a small fractions and then the conductive PMMA will be further coated onto graphene surface for effective assembling CNT array for tailored 3D network. CNT/graphene interface on both electrical and thermal conductivity will be investigated in the future.

Two graduate students and one undergraduate student were involved in this project and one journal paper is in the preparation. Our research team has successfully completed all the planned research tasks and also successfully attracted those students who are members of unrepresented groups to be involved in the state of the art nanofabrication research. The research activities successfully stimulate the interests of these students in the areas of scientific and engineering.

7. Acknowledgement

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